

**BENZYLIDENE FLUORENE OZONOLYSIS UNDER
CHEMILUMINESCENCE MIMETIC CONDITIONS IN HOMOGENEOUS
AND MICELLAR MEDIA
III: SUBSTITUENT EFFECT IN THE MICELLAR PSEUDOPHASE**

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Summary

The binding constants, mean occupation numbers per micelle, partition coefficients and per cent micellization of nine 9-(*p*-substituted) benzylidene fluorenes (*p*-nitro (i); *p*-cyano (ii); *p*-chloro (iii); *p*-bromo (iv); *p*-H (v); *p*-methyl (vi); *p*-methoxy (vii); *p*-methoxy-*m*-methyl (viii); *p*-dimethylamino (ix)) in cetyltrimethylammonium chloride and sodium dodecylsulphate were determined from the corresponding Stern-Volmer plots, with pyrene as the fluorescent probe. The ozonolysis reaction rates of the nine benzylidene fluorenes were measured in the micellar systems and, from the above partition coefficients together with the reaction rates in the bulk phase, the reaction rates in the micellar pseudophase, independent of the reaction rate in the bulk phase and the partition coefficient, were determined; the plots of these reaction rates ($\log k_{tr}$ or $\log k_{app}$) against Hammett's σ constants were linear.

1. Introduction

It has been shown in Part I [1] that on ozonolysis of nine 9-(*p*-substituted) benzylidene fluorenes (substituents: *p*-nitro (i); *p*-cyano (ii); *p*-chloro (iii); *p*-bromo (iv); *p*-H (v); *p*-methyl (vi); *p*-methoxy (vii); *p*-methoxy-*m*-methyl (viii); *p*-dimethylamino (ix)) under chemiluminescence mimetic conditions the reaction rates in homogeneous media were a linear function of Hammett's σ constants. A strong negative deviation for derivative ix was observed, however, when the reaction rates were measured fluorimetrically (apparent rates), as a result of quenching of the fluorescence of the emitter by the leaving moiety and this quenching effect was better illustrated in Part II [2]. In cetyltrimethylammonium chloride (CTAC) micellar media the above effect was further intensified as a result of encapsulation of the emitter and quencher in the micelle, resulting in closer proximity.

$\log k_{tr}$ (where k_{tr} is the true reaction rate measured spectrophotometrically in CTAC micelles) was again a linear function of Hammett's σ

constants but, in this case, three derivatives, namely i, ii and ix, showed a positive deviation which was tentatively attributed to a deeper penetration and stronger retention in the Stern layer of the micelle, resulting in higher rates for the bimolecular reaction between benzylidene fluorene and ozone, now enclosed in smaller volumes [3, 4].

To verify this assumption, we now wish to report the logarithms of the true and apparent reaction rates of benzylidene fluorene ozonolysis exclusively in the micellar pseudophase as a function of Hammett's σ constants, in both anionic and cationic micelles.

2. Experimental details

Benzylidene fluorenes i - ix were synthesized and fluorenone, ethanol and CTAC were purified as described in Part I. Pyrene was purified as described in Part II. Sodium dodecylsulphate (SDS) was recrystallized from acetone-ethanol (1:1). Acetonitrile was employed without further purification. Samples for the kinetic measurements were prepared as described in Part I. The CTAC concentration was 3×10^{-2} M and the SDS concentration was 1×10^{-1} M. The absorption maxima λ_{\max} for fluorenone in CTAC and SDS were as in Part I.

Samples for the Stern-Volmer plots were prepared as described in Part II; the pyrene concentration was 1×10^{-5} M. The pyrene excitation maximum λ_{\max} was 336 nm; the fluorescence maximum λ_{\max} was 400 nm. (The benzylidene fluorenes i - ix are not fluorescent.) The concentrations of quenchers i - ix were 8×10^{-6} - 8×10^{-5} M. Ozone was produced and employed as described in Part I. All solutions were not deaerated and all measurements were performed at room temperature.

3. Results and discussion

The micellar model employed here is that of Menger [5].

The rate constant of a pseudo-first-order reaction in micellar media such as the benzylidene fluorene ozonolysis of the present work (Part I) is given [3, 6] by

$$k_{\text{tr}} = \frac{\{(P_A - 1)Vk_{\text{tr}(m)}C\} + k_w}{1 + \{(P_A - 1)VC\}} \quad (1)$$

where k_{tr} is the reaction rate constant, in this case based on the amount of fluorenone produced and measured spectrophotometrically [1], P_A is the partition coefficient of the benzylidene fluorenes i - ix between the micellar and bulk phases, V is the partial molar volume of one "monomer" of the micelle, $k_{\text{tr}(m)}$ is the reaction rate exclusively in the micellar pseudophase, C is the surfactant concentration which actually forms micelles and k_w is the reaction rate in the bulk phase. The reaction rates exclusively in the micellar pseudophase ($k_{\text{tr}(m)}$) were obtained by solution of eqn. (1).

3.1. Calculation of C

C is the surfactant concentration employed minus the critical micelle concentration equal to 1.3×10^{-3} M for CTAC and 8.3×10^{-3} M for SDS [7]. C , thus calculated, was 2.9×10^{-2} M and 9.2×10^{-2} M for CTAC and SDS respectively.

3.2. Calculation of V

V was calculated from the equations of Tanford [8] and Mukerjee [9] as in Part I and was found to be equal to 0.243 l mol^{-1} for CTAC and 0.194 l mol^{-1} for SDS.

3.3. Calculation of k_w

k_w could not be measured in water because of the strong hydrophobic character of the benzylidene fluorenes i - ix and was measured in water-acetonitrile instead. The ozonolysis reaction rates based on fluorenone formation were measured spectrophotometrically with a technique similar to that described in Part I, in 10 - 50 vol.% water-acetonitrile [10, 11]. The k_w values thus obtained were a linear function of per cent acetonitrile; extrapolation of the plots gave the k_w values at zero acetonitrile or 100% water concentration, shown in Table 1.

3.4. Calculation of P_A

To calculate P_A , a completely micellized fluorescent probe was required, capable of being quenched by the benzylidene fluorenes i - ix. Preliminary experiments in ethanol indicated that pyrene, a fluorescent probe known to be completely micellized in CTAC and SDS micelles [12, 13], was quenched by the benzylidene fluorenes of the present work (for example, k_q in ethanol by iii is found to be equal to $1.87 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The calculations were based on eqns. (4) - (6) of Part II, now employing i - ix as quenchers of the pyrene fluorescence. The CTAC concentrations were 6×10^{-3} , 8×10^{-3} and 1×10^{-2} M, while the SDS concentrations were 1×10^{-2} , 4×10^{-2} and 7×10^{-2} M. The micellar concentrations [Mic] were calculated from

$$[\text{Mic}] = \frac{C - C_{\text{CMC}}}{N} \quad (2)$$

where C is the surfactant concentration, C_{CMC} is the critical micelle concentration and N is the aggregation number (80 for CTAC and 62 for SDS), which did not change at the surfactant concentrations employed [14] (5.88×10^{-5} , 8.33×10^{-5} and 1.09×10^{-4} M for CTAC and 2.58×10^{-5} , 5.09×10^{-4} and 9.95×10^{-4} M for SDS). Typical Stern-Volmer plots for benzylidene fluorene ix in CTAC and SDS are shown in Figs. 1 and 2; typical graphs of eqn. (6) (Part II), for ix in CTAC and SDS are shown in Figs. 3 and 4 respectively. From such plots and graphs mean occupation numbers \bar{n}_Q , binding constants K_b , and per cent micellization were calculated. These are shown in Table 2 for i - ix. When micellar volumes of 19 l and 11 l for 1 mol of CTAC and 1 mol of SDS micelles respectively [8, 15] were

TABLE 1

True reaction rate constants in water (k_w) in cetyltrimethylammonium chloride and in sodium dodecylsulphate (k_{tr}) and exclusively in the micellar pseudophase in cetyltrimethylammonium chloride and in sodium dodecylsulphate ($k_{tr(m)}$)

Fluorene	k_w (s^{-1})	k_{tr} (CTAC) (s^{-1})	$\log k_{tr}$ (CTAC)	k_{tr} (SDS) (s^{-1})	$\log k_{tr}$ (SDS)	$k_{tr(m)}$ (CTAC) (s^{-1})	$\log k_{tr(m)}$ (CTAC)	$k_{tr(m)}$ (SDS) (s^{-1})	$\log k_{tr(m)}$ (SDS)
i	9.90×10^{-4}	1.61×10^{-2}	-1.79	2.02×10^{-2}	-1.69	1.77×10^{-2}	-1.75	2.20×10^{-2}	-1.66
ii	1.11×10^{-3}	1.53×10^{-2}	-1.81	1.92×10^{-2}	-1.72	2.11×10^{-2}	-1.68	2.23×10^{-2}	-1.65
iii	1.73×10^{-3}	1.55×10^{-2}	-1.81	2.15×10^{-2}	-1.67	2.65×10^{-2}	-1.58	3.05×10^{-2}	-1.51
iv	1.74×10^{-3}	1.56×10^{-2}	-1.81	2.12×10^{-2}	-1.67	2.72×10^{-2}	-1.57	2.97×10^{-2}	-1.53
v	1.92×10^{-3}	2.03×10^{-2}	-1.69	2.69×10^{-2}	-1.57	3.24×10^{-2}	-1.99	3.82×10^{-2}	-1.42
vi	2.11×10^{-3}	2.27×10^{-2}	-1.64	3.18×10^{-2}	-1.50	3.67×10^{-2}	-1.44	4.65×10^{-2}	-1.33
vii	2.15×10^{-3}	2.40×10^{-2}	-1.62	3.51×10^{-2}	-1.45	3.83×10^{-2}	-1.42	4.94×10^{-2}	-1.31
viii	2.16×10^{-3}	2.57×10^{-2}	-1.59	3.77×10^{-2}	-1.42	4.03×10^{-2}	-1.39	5.53×10^{-2}	-1.26
ix	2.87×10^{-3}	4.05×10^{-2}	-1.39	6.10×10^{-2}	-1.21	4.91×10^{-2}	-1.31	6.81×10^{-2}	-1.17

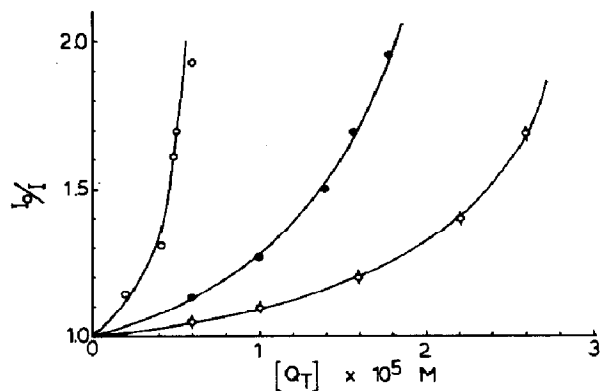
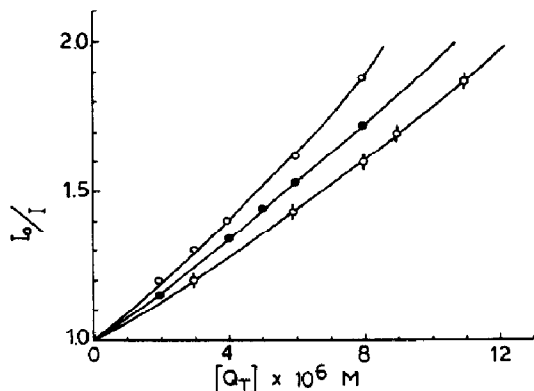


Fig. 1. Stern-Volmer plots for the quenching of pyrene by benzylidene fluorene ix at CTAC concentrations of 6×10^{-3} M (O), 8×10^{-3} M (●) and 1×10^{-2} M (◊).

Fig. 2. Stern-Volmer plots for the quenching of pyrene by benzylidene fluorene ix at SDS concentrations of 1×10^{-2} M (O), 4×10^{-2} M (●) and 7×10^{-2} M (◊).

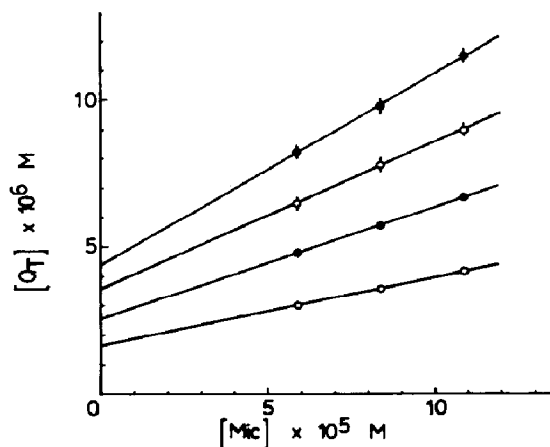


Fig. 3. Quenching of pyrene by benzylidene fluorene ix in CTAC plotted according to the equation $Q_T = \bar{n}_Q/K_b + \bar{n}_Q[Mic]$ (Part II) for various I_0/I values: O, 1.3; ●, 1.5; ◊, 1.7; ◐, 1.9.

employed, the values of P_A for i - ix were calculated and they are also shown in Table 2.

3.5. Calculation of k_{tr}

The values of k_{tr} for i - ix in CTAC under chemiluminescence mimetic conditions were obtained from Part I, Table 1. The corresponding values in SDS were similarly measured and they are given in Table 1 here, together with those in CTAC. With the above data, solution of eqn. (1) gave the values of $k_{tr(m)}$ for i - ix, which are also given in Table 1.

The plot of $\log k_{tr}$ against Hammett's σ constants for i - ix in SDS (not shown) was similar to that in CTAC (Part I) in that the same benzylidene fluorenes, namely i, ii and ix, showed a positive deviation. The fact that the

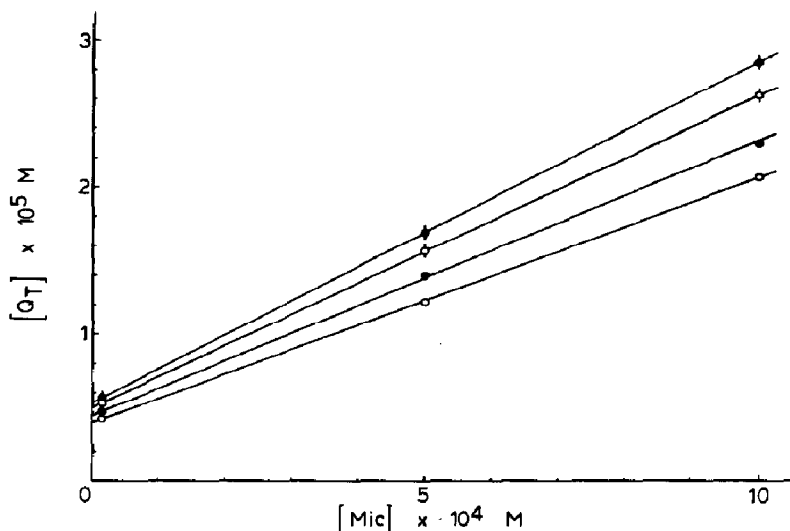


Fig. 4. Quenching of pyrene by benzylidene fluorene ix in SDS plotted according to the equation $Q_T = \bar{n}_Q/K_b + \bar{n}_Q[\text{Mic}]$ (Part II) for various I_0/I values: \circ , 1.3; \bullet , 1.5; \diamond , 1.7; \blacklozenge , 1.9.

TABLE 2

Binding K_b , mean binding constants \bar{K}_b , range of mean occupation number per micelle, mean occupation number \bar{n}_Q , mean partition coefficient \bar{P}_A and per cent micellization for benzylidene fluorenes i-ix in 3×10^{-2} M cetyltrimethylammonium chloride and 1×10^{-1} M sodium dodecylsulphate

Fluorene	Surfactant	K_b (M^{-1})	\bar{K}_b (M^{-1})	Range of \bar{n}_Q	\bar{n}_Q	P_A	Micellization (%)
i	CTAC	27690 ± 300	27690	0.66 - 2.21	1.01	1322	91
	SDS	7471 ± 400	7471	0.03 - 0.10	0.07	587	92
ii	CTAC	6466 ± 100	6466	0.06 - 0.07	0.06	337	70
	SDS	4841 ± 400	4841	0.02 - 0.05	0.04	322	88
iii	CTAC	3517 ± 100	3517	0.08 - 0.15	0.12	184	56
	SDS	1600 ± 300	1600	0.01 - 0.02	0.01	122	70
iv	CTAC	3360 ± 50	3360	0.07 - 0.15	0.13	174	55
	SDS	1560 ± 200	1560	0.01 - 0.02	0.01	127	69
v	CTAC	3350 ± 300	3350	0.02 - 0.06	0.04	208	64
	SDS	1538 ± 150	1538	0.01 - 0.04	0.03	125	69
vi	CTAC	3048 ± 400	3048	0.02 - 0.08	0.04	210	52
	SDS	1400 ± 200	1400	0.02 - 0.03	0.02	111	67
vii	CTAC	4500 ± 50	4500	0.12 - 0.18	0.16	224	62
	SDS	2019 ± 200	2019	0.01 - 0.02	0.01	127	75
viii	CTAC	3833 ± 300	3833	0.09 - 0.18	0.14	230	58
	SDS	1538 ± 100	1538	0.01 - 0.02	0.01	155	69
ix	CTAC	14860 ± 500	14860	0.03 - 0.07	0.05	779	84
	SDS	4678 ± 200	4678	0.01 - 0.03	0.02	457	87

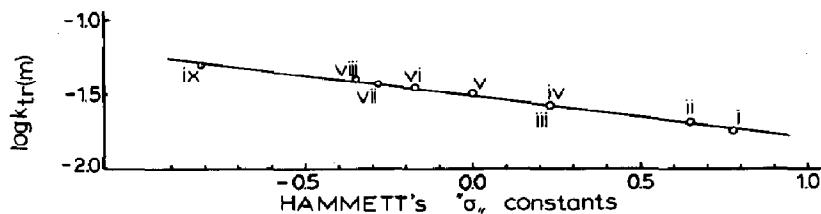


Fig. 5. Plot of $\log k_{tr(m)}$ vs. Hammett's σ constants for benzylidene fluorenes i - ix in CTAC (3×10^{-2} M).

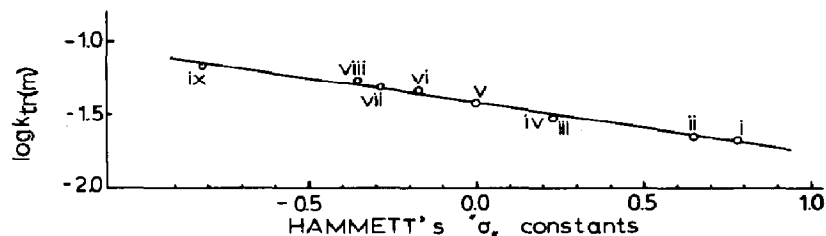


Fig. 6. Plot of $\log k_{tr(m)}$ vs. Hammett's σ constants for benzylidene fluorenes i - ix in SDS (1×10^{-1} M).

same three benzylidene fluorenes deviated both in anionic and cationic micellar media ensures that this deviation is not a matter of reaction mechanism.

Plots of $\log k_{tr(m)}$ against Hammett's σ constants (Figs. 5 and 6) indicate that the positive deviations of i, ii and ix observed in the plots of $\log k_{tr}$ against Hammett's σ constants (Part I and herein) are due to the stronger retention of these three derivatives in the Stern layer (the values of K_b and K_p for i, ii and ix should be compared with those for iii, iv, v, vi, vii and viii in Table 2), resulting in increased relative concentrations of the reactants in the micellar phase as argued in Section 1. Similar results were obtained employing the k_{tr}'' values (interrupted flow of ozone).

The results of Table 2 further support the assumption that the benzylidene fluorenes of the present work are enclosed in the Stern layer, the more polar and hydrated part of the micelle, as already established by comparison of their absorption in hexane, ethanol, ethanol-water and micelle (Part I). As benzylidene fluorenes i, ii and ix are associated with smaller relative shifts towards the absorption band in ethanol-water and micelle (Part I), it may be concluded that these are located deeper in the Stern layer than the rest of the benzylidene fluorenes.

As the three deviating benzylidene fluorenes are more polar than the rest [16, 17] they are held electrostatically deeper in the Stern layer [18] irrespective of their hydrophobic constants [19] which generally refer to partition between two phases; here the Stern layer is considered as one phase. Furthermore, from a comparison of the values of $k_{tr(m)}$ in CTAC and SDS micelles it is observed that they are higher in SDS for all the benzyli-

dene fluorenes of the present work. This is attributed to the smaller volume of SDS [20], resulting in increased relative concentrations of the reactants; the inherently smaller volumes of the SDS micelles have the same effect as the deeper penetration of the reactants in a larger micelle (CTAC), again associated with smaller volumes. The effect of the smaller volume of the SDS micelle compared with that of CTAC is also illustrated by the values of k_{tr} given in Table 1; the values in SDS are higher than those in CTAC by almost a factor of 2. In addition, although the rate of solubilization is larger in CTAC, deeper penetration of the benzylidene fluorenes is observed in SDS, established by the shifts of their absorption in SDS towards that in hexane and this is due to interactions between the benzylidene fluorene π electrons and the positively charged trimethylammonium head groups of CTAC [21].

4. Conclusions

It has now been shown that the tendency towards positive deviation of the three benzylidene fluorenes i, ii and ix in the plots of $\log k_{tr}$ and $\log k_{app}$ against Hammett's σ constants for the substituent in micellar media (Part I), which could shed doubts on the conclusions of Parts I and II, does not affect the negative deviation under study and is due to the different partition coefficients and microenvironments inside the micelle, associated with the deviating benzylidene fluorenes. Indeed, no positive deviations were observed in the plots of the logarithms of the reaction rates, both true and apparent, against Hammett's σ constants, exclusively in the micellar pseudo-phase, while the effect under study, *i.e.* the negative deviation of ix in the plot of the logarithm of the apparent rate against Hammett's σ constants, remained spectacular.

In conclusion, it has been shown in this work (Parts I, II and III) that, on ozonolysis of nine 9-substituted benzylidene fluorenes under chemiluminescence mimetic conditions, the effect of quenching of the primary emitter by the leaving fragment can be particularly pronounced as a result of the inherent proximity of the two species at the instant of their formation and these results are in agreement with previous findings on the chemiluminescence accompanying the singlet oxygen oxidation of eight substituted benzylidene acridans [22, 23]. The above quenching effect is dramatically increased when the reaction takes place in the confined space within micelles.

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